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(54) **UTILISATION D'ALCOOLS OLEOPHILES SELECTIONNES, DANS DES FLUIDES DE FORAGE A BASE D'EAU DE TYPE EMULSION HUILE-EAU; FLUIDES DE FORAGE AINSI OBTENUS, PLUS ACCEPTABLES DU POINT DE VUE ENVIRONNEMENTAL**

(54) **USE OF SELECTED OLEOPHILIC ALCOHOLS IN WATER-BASED DRILLING FLUIDS OF THE O/W EMULSION TYPE AND CORRESPONDING DRILLING FLUIDS WITH IMPROVED ECOLOGICAL ACCEPTABILITY**

(57) The use is disclosed of at least substantially water-insoluble mono-and/or polyfunctional alcohols of natural and/or synthetic origin which are fluid and/or at least plastically deformable at working temperature and have flash points of at least 80°C, or corresponding solutions of mono- and/or polyhydric alcohols in ecologically acceptable water-insoluble oils as the dispersed oil phase of water-based O/W-emulsion drilling fluids, which are suitable for an environmentally-acceptable development of geological formations and which, if desired, contain insoluble, finely particulate weighting agents for the formation of water-based O/W-emulsions drilling muds and/or further additives, such as emulsifiers, fluid-loss additives, wetting agents, alkali reserves and/or auxiliary substances for the inhibition of drilled rock of high water-sensitivity.

ABSTRACT

The use is disclosed of at least substantially water-insoluble mono- and/or polyfunctional alcohols of natural and/or synthetic origin which are fluid and/or at least plastically deformable at working temperature and have flash points of at least 80°C, or corresponding solutions of mono- and/or polyhydric alcohols in ecologically acceptable water-insoluble oils as the dispersed oil phase of water-based O/W-emulsion drilling fluids, which are suitable for an environmentally-acceptable development of geological formations and which, if desired, contain insoluble, finely particulate weighting agents for the formation of water-based O/W-emulsions drilling muds and/or further additives, such as emulsifiers, fluid-loss additives, wetting agents, alkali reserves and/or auxiliary substances for the inhibition of drilled rock of high water-sensitivity.

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Use of selected oleophilic alcohols in water-based drilling fluids of the O/W-emulsion type and corresponding drilling fluids with improved ecological acceptability

The invention discloses new drilling fluids based on water-based O/W-emulsions and O/W-emulsion drilling muds based thereon, which are distinguished by high ecological acceptability and at the same time good standing and application properties. An important area of use for the new drilling fluid systems is in off-shore wells for the development of petroleum and/or natural gas deposits, the aim of the invention being particularly to make available industrially usable drilling fluids with high ecological acceptability. The use of the new drilling fluid systems admittedly has particular significance in the marine environment, but is not limited thereto. The new mud systems can also be put to quite general use in land-based drilling, i.e. also for the development of petroleum and/or natural gas deposits here. They are, however, new valuable working agents, for example, also in geothermal wells, in water bore-holes, in the drilling of geoscientific bores and in drilling for the mining industry. It is also essentially true here that the associated ecotoxic problems are substantially simplified by the new water-based O/W-drilling fluids selected according to the invention.

The Prior Art

Fluid mud systems used in the sinking of rock bores for bringing up the loosened drill cuttings are known to be flowable systems, thickened to a limited extent, which can be assigned to one of the three following classes:

Purely aqueous drilling fluids; drilling mud systems based on oil, which as a rule are used in the form of so-called invert emulsion muds, and represent preparations of the W/O-emulsion type in which the aqueous phase is distributed as a heterogeneous fine dispersion in the continuous oil phase. The third class of the known drilling fluids is composed of water-based O/W-emulsions, i.e. fluid systems which contain a heterogeneous, finely-dispersed oil phase in a continuous aqueous phase. The invention discloses improved systems of this latter type.

The application properties of the drilling fluids of such O/W-emulsion systems take an intermediate position between the purely aqueous systems and the oil-based invert fluids. The advantages, but also the disadvantages, of the purely aqueous systems are connected with the advantages and disadvantages of the oil-based invert-emulsions disclosed hitherto. Detailed information on this subject can be found in the relevant specialist literature, refer, for example, to the text book by George R. Gray and H.C.H. Darley, "Composition and Properties of Oil Well Drilling Fluids", 4th. edition, 1980/1981, Gulf Publishing Company, Houston, and the extensive specialist and patent literature cited therein and to the manual "Applied Drilling Engineering", Adam T. Bourgoyne, Jr. et al., First Printing Society of Petroleum Engineers, Richardson, Texas (USA).

One of the main weaknesses of purely water-based drilling mud systems lies in the interaction of water-sensitive, particularly water-swellable, rock and/or salt formations with the aqueous drilling fluid and the secondary effects initiated thereby, in particular bore-hole instability and thickening of the drilling fluid. Many proposals are concerned with the reduction of this range of problems and have, for example, resulted in the development of the so-called inhibitive water-based muds, cf. for example, "Applied Drilling Engineering", loc. cit., Chapter 2, Drilling Fluids, 2.4 and Gray and Darley loc. cit., Chapter 2, in particular the sub-section on pages 50 to 62 (Muds for "Heaving Shale", Muds for Deep Holes, Non-Dispersed Polymer Muds, Inhibited Muds: Potassium Compounds).

In more recent practice, in particular drilling fluids based on oil, which consist of the 3-phase system oil, water and finely particulate solids and are preparations of the W/O-emulsion type, have succeeded in overcoming the difficulties described above. Oil-based drilling fluids were originally based on diesel oil fractions containing aromatics. For detoxification and to reduce the ecological problems created thereby, it was then proposed to use hydrocarbon fractions which are largely free of aromatics - now also known as "non-polluting oils" - as the continuous oil phase, see in this regard, for example, the publications by E.A. Boyd et al. "New Base Oil Used in Low Toxicity

Oil Muds", Journal of Petroleum Technology, 1985, 137 - 143 and R.B. Bennet "New Drilling Fluid Technology - Mineral Oil Mud", Journal of Petroleum Technology, 1984, 975 - 981 and the literature cited therein.

The drilling fluids of the water-based O/W-emulsion system type have also hitherto used pure hydrocarbon oils as the dispersed oil phase, cf. here, for example, Gray, Darley loc. cit., p. 51/52 under the section "Oil Emulsion Muds" and the tabular summary on p. 25 (Tables 1-3) with details for water-based emulsion fluids of the salt-water mud, lime mud, gyp mud and CL-CLS mud type.

In this context in particular it is known that water-based O/W-emulsion fluids represent a substantial improvement in many regards to the purely water-based drilling mud systems. Particularly in more recent times, however, the advantages and disadvantages of such water-based emulsion fluids have also been examined critically in comparison with the oil-based invert-systems. This is due to the considerable ecological reservations now felt towards the oil-based invert drilling fluids commonly used today.

These ecological reservations can be subdivided into two problem areas:

In addition to the basic constituents oil and water, all drilling fluid systems based on water and/or oil require a large number of additives for establishing the desired application properties. The following can be mentioned here purely by way of example: emulsifiers or emulsifier systems, weighting agents, fluid-loss additives, wetting agents, alkali reserves, viscosity regulators, in some cases auxiliary agents for the inhibition of drilled rock with high water-sensitivity, disinfectants and the like. A detailed summary can be found, for example, in Gray and Darley, loc. cit., Chapter 11, "Drilling Fluid Components". The industry has developed additives which currently appear ecologically harmless, but also additives which are ecologically questionable or even ecologically undesirable.

The second problem area is determined by the oil phases used in such drilling fluids. Even the hydrocarbon fractions which are largely free from aromatics, currently known as "non-polluting oils", are not

completely harmless when released into the environment. A further reduction in the environmental problems - caused by the fluid oil phases of the type referred to here - appears urgently necessary. This is true in particular for the sinking of off-shore wells, e.g., for the development of petroleum or natural gas deposits, because the marine eco-system reacts particularly sensitively to the introduction of toxic and poorly degradable substances.

There have recently been some proposals for reducing these latter problems. For example, the US Patent Specifications 4,374,737 and 4,481,121 disclose oil-based invert-drilling fluids in which non-polluting oils are to be used. The following can be mentioned together as of equal value as non-polluting oils: mineral oil fractions which are free from aromatics and vegetable oils, such as groundnut oil, soybean oil, linseed oil, corn oil, rice oil or even oils of animal origin, such as whale oil. These named ester oils of vegetable and animal origin are all, without exception, triglycerides of natural fatty acids, which are known to have high environmental acceptability and are clearly superior from the ecological point of view to hydrocarbon fractions - even when these do not contain aromatic hydrocarbons.

In the above US Patent Specifications, however, not one concrete example describes the use of such natural ester oils in invert drilling fluids. Without exception mineral oil fractions are used as the continuous oil-phase. In fact, oils of vegetable and/or animal origin of the type mentioned are not considered for invert drilling fluids for practical reasons. The rheological properties of such oil phases cannot be controlled over the wide temperature range generally required in practice, from 0 to 5°C on the one hand, up to 250°C and more on the other.

<u>The Applicant's other proposals</u>

A series of co-pending Applications by the Applicant describes the use of easily biodegradable and ecologically harmless ester oils as the continuous oil phase in W/O-invert drilling mud systems. Refer here in particular to the co-pending Canadian

Applications 2,006,009 and 2,006,010, filed December 19, 1989, and the modifications of the ester oils that can be used as in the details of the co-pending Canadian Applications 2,047,697 and 2,047,706, filed March 1, 1990.

The subject of these co-pending Applications is the use of ester oils based on selected monocarboxylic acids and monocarboxylic acid mixtures and monofunctional and optionally polyfunctional alcohols as the continuous oil phase in W/O-invert systems. The co-pending Applications show that, using the esters and ester mixtures disclosed therein, not only can satisfactory rheological properties be established in the fresh drilling fluid, but it is also possible by the additional use of selected, known alkali reserves in the drilling fluid, to work without fearing undesired thickening effects when there is partial ester hydrolysis.

A modified form of such W/O-invert drilling mud systems is described in the Applicant's co-pending Canadian Application 2,051,624, filed March 29, 1990. This describes the use of

a) mono- and/or polyfunctional alcohols of natural and/or synthetic origin which are at least largely water-insoluble and are fluid and pumpable in the temperature range of 0 to 5°C

or of

b) solutions, which are fluid and pumpable in the given temperature range, of at least largely water-insoluble mono- and/or polyfunctional alcohols of natural and/or synthetic origin in ecologically acceptable water-insoluble oils

as the continuous oil phase in drilling fluids which are in the form of W/O emulsions and in the alcohol-containing oil phase have a dispersed aqueous phase and also, if desired, further conventional additives. As the ecologically acceptable, water-insoluble oils for admixture with the water-insoluble alcohols, at least some ester oils are provided as described in the Applicant's co-pending Applications cited above.

An important further development of such invert drilling fluids based

on ester oils is the subject of the Applicant's co-pending Application 2,009,689, filed February 9, 1990.

The teaching of this co-pending Application starts with the concept of also using in invert drilling fluids based on ester oils a further additive which is suitable for keeping the desired rheological data of the drilling fluid in the required range, even when in use larger and larger amounts of free carboxylic acids are formed by partial ester hydrolysis. The Application provides for the additional use of basic amine compounds, which are capable of forming salts with carboxylic acids and have a marked oleophilic nature and at most limited water-solubility, as additives in the oil phase.

The invention problem and its technical solution

The present invention starts with the problem of providing drilling mud systems of the highest, and in this form previously unknown, ecological acceptability which simultaneously have good application properties and also make satisfactory use possible in problem areas in particular. The invention thus consciously wishes to reject the oil-based type of invert drilling mud systems and to return to the oil-modified water-based type of O/W-emulsion systems. The auxiliary agents described in the cited co-pending Applications of the Applicant, and the ecological advantages associated therewith, are now, however, also to be used in this class of drilling mud systems.

In a first embodiment, the aim of the invention is therefore to make use of the advantages of O/W-emulsion mud systems against purely water-based drilling fluids, but at the same time to replace the mineral-oil phase at least to a substantial amount - completely or in part - with ecologically harmless alcohols of a marked oleophilic character.

In a further approach, the invention aims also to moderate the ecological concerns of the second problem area, associated with the additives and auxiliary agents in drilling fluids, by selecting from the wide range of additives known in this field, at least to a large extent and preferably universally, those auxiliary agents which are distinguished by their ecologically harmless nature.

The subject of the invention is accordingly in a first embodiment the use of at least largely water-insoluble mono- and/or polyfunctional alcohols of natural and/or synthetic origin which are fluid and/or at least plastically deformable at working temperature and have flash points of at least 80°C, or corresponding solutions of mono- and/or polyhydric alcohols in ecologically acceptable water-insoluble oils as the dispersed oil-phase of water-based O/W-emulsion drilling fluids, which are suitable for an environmentally acceptable development of geological formations, and, if desired, contain insoluble, finely particulate weighting agents for the formation of water-based O/W-emulsion drilling muds and/or further additives, such as emulsifiers, fluid-loss additives, wetting agents, alkali reserves and/or auxiliary substances for the inhibition of drilled rock with high water-sensitivity.

In a further embodiment, the invention relates to water-based O/W-emulsion drilling fluids, which in a homogeneous aqueous phase contain, in stable dispersion, an oil phase in amounts of about 5 to 50 % by weight - the percentage by weight referred to the sum of the unweighted water phase and oil phase - together, if required, with dissolved and/or dispersed auxiliary substances, such as emulsifiers, fluid-loss additives, wetting agents, finely particulate weighting agents, salts, alkali reserves and/or disinfectants, and are characterized in that at least a substantial part of the dispersed oil phase is formed by water-dispersible mono- and/or polyfunctional alcohols of natural and/or synthetic origin which are fluid or at least plastically deformable at working temperature, and have flash points of at least 80°C, or corresponding solutions of mono- and/or polyhydric alcohols in ecologically acceptable, water-insoluble oils.

Both embodiments of the teaching according to the invention include the additional preferred step of also using for the water-based emulsion drilling fluids or emulsion drilling muds, at least to a large extent, those inorganic and/or organic auxiliary and loading substances which are at least predominantly ecologically and toxicologically harmless. And thus, for example, in the most important embodiments of the invention the use of auxiliary agents based on soluble toxic heavy-

metal compounds is avoided.

The preferred embodiments of the invention

The mixture ratios of the alcohol/water phases cover the usual range for previously known O/W-emulsion drilling fluids based on mineral oils. The lower limit values for the oil phase are usually at least about 5 % by weight, or preferably between about 5 and 10 % by weight, e.g., therefore 7 or 8 % by weight - each percentage by weight referred to the total weight of the fluid oil phase and water phase, each in the unweighted state. Minimum amounts of the order given ensure that use can be made of the characteristic peculiarities of an O/W-emulsion fluid. The upper limit value for the oil content is usually about 50 % by weight or even slightly higher, e.g., a maximum of about 65 % by weight. Assuming that the droplet size of the dispersed oil phase is sufficiently even, the range of most dense packing is then already achieved, and therefore conversion into the fluid type of the W/O-invert fluids is obvious or appears logical.

The upper limit for the content of dispersed oil phase in the O/W-fluids according to the invention is generally determined by cost/benefit considerations and is, for example, about 45 % by weight, preferably less, e.g., about 40 % by weight.

An alcohol amount from about 10 to 40 % by weight - percentage by weight calculated as before - and in particular amounts of alcohol phase from about 15 to 35 % by weight offer the possibility of making use of many - known and not previously described - advantages of such emulsion fluids. Oil contents of, for example, 20 % by weight, or in an extreme case, 30 % by weight provide the basis of high-quality drilling fluids which at least very closely approach the oil-based invert fluids in the way they function, but require very much less alcohol or ester-oil phase.

The various embodiments of the invention

In a first embodiment the dispersed oil phase of the water-based O/W-drilling fluids is formed exclusively, or to much the largest part, by

the essentially water-insoluble and preferably markedly oleophilic alcohols. The rheology of the alcohols used is adapted here to the technical requirements of the drilling fluids, slight rheological corrections are possible by adding the small amounts of diluents provided in this embodiment. In the case described here, consideration can be given in particular to dispersed oil phases which are formed to more than 70 % by weight, preferably to more than 80 % by weight and, if required, exclusively by the alcohols themselves.

The oil-mixture components optionally added in small amounts in this embodiment can be pure hydrocarbon compounds, particularly those free from aromatics, but in particular selected ester oils of the type described in the above co-pending Applications of the Applicant. This embodiment will be discussed in more detail below.

A second embodiment of the invention relates to the use of dispersed oil-phases in systems of the type referred to here, which have considerable or even predominant amounts of non-water-miscible oils, which are not identical with the oleophilic alcohols, but are present in admixture with them.

In this embodiment, the content of the alcohols selected according to the invention in the dispersed oil phase is from at least about 10 % by weight to about 70 % by weight - each referred to the fluid oil phase - in which alcohol parts in amounts of at least about 35 % by weight, and preferably at least about 50 % by weight, of the oil phase can be preferred. Ecologically harmless ester oils of the type to be described in detail below are preferred mixture components of this second embodiment also. The additional use of pure hydrocarbon oils is not, however, excluded.

The invention relates finally, in a third variant, to the use of practically water-insoluble alcohols in particular of a marked oleophilic character as an additive in the oil phase which is present in lower amounts - usually in the range of about 0.1 to a maximum of 10 % by weight, referred to the oil phase -, to give the dispersed oil phase selected important added properties. Again in a preferred embodiment, the largest part of the oil phase is formed here by ester

oils of the type described below.

The alcohol components of marked oleophilic character used according to the invention

The use of alcohols as the oil phase, but also their combined use in smaller or larger amounts in the oil phase, requires that these alcohol components are sufficiently insoluble in water. The water-solubility of suitable alcohols at room temperature is preferably less than 5 % by weight, in particular less than 1 % by weight, and preferably not more than about 0.5 % by weight.

The following general rules apply for the chemical nature of the alcohols: Monofunctional and/or polyfunctional alcohols are suitable, provided that the oleophilic character of the alcoholic component is maintained. In particular, as well as the monofunctional alcohols, difunctional compounds and/or partial ethers of polyfunctional alcohols with at least one free hydroxyl group can be considered. The alcohols themselves should be ecologically acceptable and thus in the preferred embodiment should have no aromatic constituents. The preferred compounds are straight-chain and/or branched aliphatic or also corresponding unsaturated, in particular mono- and/or poly-olefin-unsaturated alcohols. Cycloaliphatic alcohols can be considered.

An important general requirement for the use of the invention is that these alcohols as such are not only ecologically acceptable, but also do not cause any other toxicological hazards, particularly on inhalation. Alcohols with a marked oleophilic nature, as required according to the invention, are in any case usually distinguished by such a low volatility that this requirement is satisfied without any difficulties.

The following should also be noted for the admixture of the alcohols used in the invention with ester oils: The free alcohols used according to the invention may be the same or different from the alcohol components which are used in the ester oil.

While the alcohol component in the ester oils is determined, for

example, by considerations of the rheology of the ester oil and/or of the availability of the ester-forming alcohols, the use of the free alcohols in the invention is proposed in order to achieve the desired improvements in the emulsion drilling fluid.

In particular, alcohols with a straight-chain and/or branched hydrocarbon structure can be considered from the wide range of markedly oleophilic alcohols, particularly in the embodiment in which the alcohols themselves form at least the main part of the dispersed oil phase. Within the limits set for the corresponding monofunctional alcohols, corresponding compounds with at least 5, preferably at least 6 or 7 carbon atoms, are suitable compounds, with corresponding alcohols with at least 8 carbon atoms in the molecule being particularly suitable for use. The upper limit of the carbon number is determined by industrial availability and is, for example, around 36, preferably from about 20 to 24. The alcohols themselves can be straight-chain and/or branched, they can be aliphatic-saturated or even mono- and/or poly-olefin-unsaturated.

The rheological properties of the alcohols are largely determined by their structure in a manner known per se. Saturated and straight-chain alcohols are more quickly prone to thickening or solidification than olefin-unsaturated and/or branched alcohols. For example, saturated straight-chain fatty alcohols with from 16 to 18 carbon atoms are known to have solidification ranges around 50°C, while the olefin-unsaturated oleyl alcohol solidifies below 4°C.

In principle, alcohols of natural and/or synthetic origin are suitable. In particular, the synthetic alcohols in the range which is of particular interest here, about 8 to 24 carbon atoms, which can also contain unsaturated parts, are frequently low-cost components available commercially and can be put to use for the purposes of the invention.

The alcohols themselves should have flash points of at least 80°C here, preferably of at least 100 °C and in particular of at least 120°C. In addition to the named monofunctional alcohols with preferably at least 8 carbon atoms, selected polyols or their partial ethers can also be considered here. Suitable polyols are in particular optionally

branched-chain diols with an adequate amount of the oleophilic hydrocarbon radical in the molecule. For example, oleophilic diols with hydroxyl groups in the alpha,omega position and/or diols with their hydroxyl groups on adjacent carbon atoms are suitable. Characteristic examples of such compounds are the 2,2-dimethyl-1,3-propanediol (neopentylglycol) or the saponification products of epoxidized olefins. In particular, partial ethers of such diols with monofunctional alcohols can, however, also be considered.

There is increasing freedom in the selection of suitable alcohol components, particularly in the embodiments in which the dispersed oil phase is formed largely by water-insoluble mixture components, in particular therefore by the ester oils to be described below. Among others, at least largely water-insoluble polyalkyleneglycolethers and corresponding mixed ethers of lower alkylene glycols have proved to be usable additives here. For example, corresponding mixed ethers of ethylene oxide and/or propylene oxide are therefore usable additives in the sense of the invention even when they attain molecular weights of, e.g. 5000 and at the same time exhibit sufficient water-insolubility in the total system. Compounds of the latter type are significant particularly in the embodiment which has as its subject the addition of water-insoluble alcohols as the additive in a maximum amount of about 10 % by weight.

In an important embodiment of the invention water-insoluble alcohols are used which on their part are free from basic amino groups and preferably also do not contain any other reactive groups, for example, carboxyl groups.

<u>The mixture components in the dispersed oil-phase</u>

Suitable oil components for the admixture according to the invention are the mineral oils currently used in practice in drilling fluids, and preferably the aliphatic and/or cycloaliphatic hydrocarbon fractions which are essentially free from aromatics. Refer here to the relevant prior-art publications and the commercial products available on the market.

Particularly important mixture components, however, for the invention are ester oils which are ecologically acceptable, with the following general considerations being of initial importance:

The ester oils should be fluid at ambient temperature, but also under their conditions of use, with the fluidity range, however, also including those materials which are at least plastically deformable at ambient temperature and which soften to become fluid at the usually high working temperatures. For reasons of easier processability, ester oils are preferred in practice with solidification values (pour point and setting point) below 10°C and usefully below 0°C. Corresponding ester oils with solidification values not above -5°C can be particularly suitable. It should be taken into account here that the drilling fluids are usually produced on site using, for example, sea water at comparatively low water-temperatures.

For reasons of industrial safety, it must be required that the ester oils have flash points of at least 80°C, however, higher flash points of at least 100°C and substantially higher values are preferred, for example, those above 150 or 160 °C.

A further important requirement for the optimal employment of the subject of the invention is that the ester oils have a biologically or ecologically acceptable constitution, i.e. in particular are free from undesired toxic constituents. In the preferred embodiment of the invention, ester oils are accordingly used which are free from aromatic constituents and in particular have saturated and/or olefin-unsaturated, straight-chain and/or branched hydrocarbon chains. The use of components containing cycloaliphatic structural constituents is possible from ecological points of view, but for reasons of cost will be of less significance in practice.

Carboxylic acid esters of the type in question here are subject, as the highly dispersed oil-phase in a continuous aqueous phase, to a limited degree to hydrolytic ester-cleavage with liberation of the ester-forming constituents carboxylic acid and alcohol. Two closely linked issues should be taken into account as regards the application properties of the ester oils in the sense of the invention, namely

considerations of the possible inhalation-toxicity of the liberated components, in particular of the alcohol components, and also the change in the composition of the emulsion fluid and the associated possible change in its application properties.

For comprehension of the teaching according to the invention, these considerations should be examined separately for each of the ester-forming basic constituents - on the one hand the alcohols and on the other the carboxylic acids.

According to the invention, both monohydric alcohols and polyhydric alcohols are suitable as the ester-forming alcohol components, and any mixtures of these types can also be used. A further distinction can be made between alcohols from the consideration of their solubility behavior in water. Alcohols can be water-soluble and/or water-insoluble.

In a first group, polyhydric alcohols are to be considered. Preferred here are in particular the industrially easily available lower, polyfunctional alcohols with 2 to 5, preferably 2 to 4 hydroxyl groups and in particular 2 to 6 carbon atoms, which form esters with a suitable rheology.

Characteristic representatives are ethylene glycol, the propanediols and in particular glycerin.

Polyhydric alcohols of the type referred to here are distinguished by high water-solubility and at the same time by such low volatilization values that considerations of the exclusion of toxic hazards on inhalation are usually not applicable.

Polyhydric lower alcohols of the type referred to here can be used as totally esterified oil components and/or as partial esters with some free hydroxyl groups and/or can be formed in the practical use of the emulsion fluid according to the invention. Provided that the partial esters formed retain the at least largely water-insoluble character of the oil phase, no substantial change takes place as regards the oil/water ratio in the emulsion fluid. The situation is only different

when water-soluble hydrolysis products form - in particular therefore the free lower polyhydric alcohols. The changes which occur in practical operation in such emulsion fluids from this cause are, however, insignificant. Firstly, a comparatively high stability of the ester bond is ensured under the working conditions according to the invention. O/W-emulsion fluids are known to operate usually in the pH-range of around neutral to moderately alkaline, for example, in the pH-range of about 7.2 to 11 and in particular about 7.5 to 10.5, so that for these considerations alone there is no aggressive hydrolytic attack on the ester bond. In addition, and moreover, the following is in particular also true:

In the practical use of the drilling fluid, and the associated driving forward of the bore into ever deeper earth strata, there is a continual consumption of the drilling fluid and in particular of the oil-phase used in the drilling fluid. Emulsion fluids are known - and this is an important point of value in their use - for the fact that the emulsified oil phase clings on to solid surfaces and therefore both effects the sealing of the filter bed to the wall of the bore shaft and hinders, or even prevents, interaction between the drilled rock and the aqueous phase of the drilling fluid. This continual consumption of drilling fluid, and in particular of the oil-phase necessitates a continual supply of oil-based mud. In practical operation, a state of equilibrium is therefore rapidly established in the drilling fluid which prevails over, and makes possible, a continuous operation for long periods of time.

The considerations introduced above are naturally only significant in the context of the invention when not inconsiderable amounts of the dispersed oil phase are formed by added ester oils. The oleophilic alcohols, and their admixture with hydrolysis-resistant mixture constituents, are not affected by such additional considerations and therefore even when ester oils are largely or even completely omitted, this can be seen as an important and preferred embodiment of the use according to the invention.

In some points of view, further considerations should be taken into account when monohydric alcohols are used as an ester-forming

constituent of the ester oils. Here only the lower representatives of these alcohols are water-soluble or, in an unlimited amount, water-miscible. In addition, however, volatility is a not unimportant consideration in the case of these alcohols. In the practical operation of a bore, at least moderately increased temperatures are rapidly established in the circulated drilling fluid so that the parts exposed by pumping to remove the drill cuttings have a temperature, for example, in the range of 50 to 70 °C. Considerations of the toxicological effects on inhalation must therefore be taken into account here. Even C_4-alcohols, for example, isobutyl alcohol, can be so volatile under the operating conditions on the drilling platform that hazards to personnel must be taken into account. According to the invention, therefore, when ester oils are employed together with monohydric alcohols, the lower carbon number limit for these monohydric alcohols is preferably selected as 6, and work carried out with esters of monofunctional alcohols with at least 8 carbon atoms can be particularly preferred.

The selection and limitation of the carbon number in the ester-forming alcohol, however, then at the same time gives the following result as regards the composition of the ester-oil phase when taking into account a partial hydrolysis during operation: The hydrolyzing parts of such ester oils are converted to the free alcohol which remains as a practically water-insoluble mixture constituent in the dispersed ester-oil phase.

It is possible within the framework of the teaching according to the invention to use identical alcohols here in both the free form and in the ester oil also used, it is not, however, necessary. The invention therefore also includes embodiments in which alcohols are formed through ester hydrolysis which differ from the existing free alcohol content originally used.

A number of points must also be considered with regard to the carboxylic acids formed by the partial hydrolysis of the ester oils also used.

Here it is possible, depending on the specific constitution of the

carboxylic acids used, to distinguish between two basic types - without a rigid transition: carboxylic acids which give rise to carboxylic acid salts with an emulsifier effect, and those which give rise to inert salts.

The respective chain-length of the liberated carboxylic acid molecule is decisive here in particular. Moreover, the salt-forming cation usually present in the alkali reserves of the drilling fluid should also be considered.

In general the following rules apply: Lower carboxylic acids, for example those with 1 to 5 carbon atoms, give rise to the formation of inert salts, for example, the formation of corresponding acetates or propionates. Fatty acids of higher chain-length and in particular those with from 12 to 24 carbon atoms result in compounds with an emulsifier effect.

By selecting suitable ester oils - and to a certain extent also the salt-forming cations in the emulsion fluid - the specific control of the secondary products in the emulsion fluid is therefore possible, which can also have considerable influence on the nature and effect of the emulsion fluid. What has previously been stated also applies here: It is not only the dispersed organic phase, but also the aqueous phase, which is subject to continual consumption in practice and thus requires replacement. In stationary operation, therefore, rapidly controllable states of equilibrium will be established, even with regard to the reaction by-products based on the ester-forming carboxylic acids as discussed here.

General details for the definition of suitable ester oils

In the sense of the invention, the corresponding reaction products of monocarboxylic acids with monofunctional and/or polyfunctional alcohols of the type given are preferred as the ester oils. The additional use of polyvalent carboxylic acids is not, however, excluded, but they are of less significance, in particular for reasons of cost.

The carboxylic acids here can be of natural and/or synthetic origin,

they are, as already indicated, preferably straight-chain and/or branched and optionally cyclic, but not aromatic in structure. The ester-forming carboxylic acids can be saturated and/or unsaturated, with unsaturated compounds here being understood, in particular, to be olefin-unsaturated compounds, which can be mono- but also poly-olefin-unsaturated. Olefin-unsaturated components can be of particular significance for adjusting the predetermined rheology values. It is known that olefinic longer-chain compounds are suitable as corresponding saturated components for the formation of esters with lower melting points.

The preferred range for the carbon number of the carboxylic acids extends from 1 to 36 and in particular from 2 to 36. For reasons of easy availability, an upper limit for the carbon number can be about 22 to 24. The selection of the respective chain length in the ester-forming carboxylic acid components takes place - depending on the nature of the alcohols component(s) used - under consideration of the various issues already discussed, and refer not only, for example, to the ester and/or its rheology directly, but also to the reaction by-products formed in particular by partial hydrolysis.

Suitable alcohols are, as indicated, both monofunctional alcohols - taking into consideration of the limitations listed above - and polyfunctional alcohols, particularly lower polyfunctional alcohols with 2 to 6 carbon atoms and preferably with a maximum of 4 hydroxyl groups.

The alcohol components here can also be of natural and/or synthetic origin, they are straight-chain or branched and in particular in the case of the monofunctional alcohols are saturated and/or also olefin-unsaturated. Monofunctional alcohols have in particular up to 36 carbon atoms, preferably up to about 24 carbon atoms. Alcohols with 6 to 18, in particular 7 to 15 carbon atoms, of natural and/or synthetic origin can only be of particular significance in the formation of the ester oils.

Particularly important ester oils in the sense of the use in the invention are the ecologically-acceptable ester oils as described in

particular in the cited co-pending Applications 2,006,009; 2,006,010; 2,047,697 and 2,047,706. For completion of the invention disclosure, essential characteristics of such ester oils or ester mixtures are briefly summarized in the following.

The dispersed ester-oil phase accordingly contains carboxylic acid esters from at least one of the following sub-classes:

a) Esters from C_{1-5}-monocarboxylic acids and mono- and/or polyfunctional alcohols, in which radicals from monohydric alcohols have at least 6, preferably at least 8 carbon atoms, and the polyhydric alcohols preferably have 2 to 6 carbon atoms in the molecule,
b) esters from monocarboxylic acids of synthetic and/or natural origin with 6 to 16 carbon atoms, in particular esters of corresponding aliphatic-saturated monocarboxylic acids and mono- and/or polyfunctional alcohols of the type indicated under a),
c) esters of olefin mono- and/or poly-unsaturated monocarboxylic acids with at least 16, in particular 16 to 24 carbons atoms, and in particular monofunctional straight-chain and/or branched alcohols.

The latter esters of olefinic mono- and/or poly-unsaturated monocarboxylic acids with at least 16 carbon atoms (c) are preferably assigned to at least one of the following sub-classes:

c1) esters which are derived by more than 45 % by weight, preferably by more than 55 % by weight from di- and/or poly-olefin-unsaturated C_{16-24}-monocarboxylic acids,
c2) esters which are derived by not more than 35 % from di- and poly-olefin-unsaturated acids, and are preferably at least about 60 % by weight mono-olefin-unsaturated.

The raw materials for obtaining many of the monocarboxylic acids in these sub-classes, in particular those with a higher carbon number, are vegetable and/or animal oils. Coconut oil, palm kernel oil and/or babassu oil, can be mentioned in particular as materials used for

obtaining monocarboxylic acids predominantly in the range of up to 18 carbon atoms, and with essentially saturated components. Examples of vegetable ester oils, in particular for olefinic mono- and optionally poly-unsaturated carboxylic acids with from 16 to 24 carbon atoms, are palm oil, peanut oil, castor oil and in particular rapeseed oil. Carboxylic acids of animal origin of this type are in particular corresponding mixtures of fish oils, such as herring oil.

The teaching of the invention expressly includes also and in particular the use of monocarboxylic acid triglycerides and therefore in particular also the use of corresponding glyceride oils of natural origin. Here, however, the following must be considered: Natural oils and fats usually occur in a form so highly contaminated, for example, with free carboxylic acids or other accompanying substances, that there is as a rule no question of immediately processing them in O/W-emulsion fluids of the type referred to here. If such natural materials are added in the commercially available form to water-based drilling fluids, then almost immediately, such a large amount of foam forms in the drilling fluid being used as to constitute a serious hindrance or even to result in the drilling fluid being unusable. This may not be the case if cleaned and/or synthetically obtained selected triglycerides are used in the dispersed oil phase. The teaching according to the invention can be realized without exception in this respect. In principle, however, with such esters of high-grade alcohols one must always anticipate a not inconsiderable tendency to foam formation. Partial esters of glycerin - the mono- or di-glycerides - are known to be effective emulsifier components.

As already indicated, it is not only the comparatively low-viscosity ester oils as in the disclosure of the cited earlier Applications of the Applicant in the field of invert drilling fluids, based on ester-oils, which are suitable for the purposes of the invention, but within the framework of O/W-emulsion fluids, in particular comparatively viscous ester oils can be of advantage as components of the dispersed phase. They are, for example, valuable auxiliary agents for sealing of the finest pores in the filter cake of the bore shaft, or in rendering inert swellable rock, the lubricating ability of such ester oils of comparatively high viscosity even at elevated temperatures in the bore

shaft, and in particular also in deviated bore-holes, is in some cases distinctly better than the comparatively low-viscosity ester oils. A dispersed ester oil phase of comparatively high-viscosity ester oils does not cause any detrimental effect on the drill-technology, the rheology of the system as a whole is determined by the continuous aqueous phase. In this sense it may be preferred to use ester oils as the dispersed phase which have a Brookfield viscosity of up to about 500,000 mPa.s, preferably up to about 1 million mPa.s or even higher, for example, up to about 2 million mPa.s (determined at room temperature). This constitutes an important extension of the teaching in the noted co-pending Applications of the Applicant in the field of oil-based invert drilling fluids based on ester-oils.

In one embodiment of the invention, branched-chain components and in particular alpha-branched-chain alcohols and/or carboxylic acids can be of particular significance. Branches of this type are known on the one hand to influence the rheology, usually the esters formed by such a chain-branching are more mobile. Moreover, such alpha-branching can, however, also have work towards increased hydrolysis stability under working conditions, use of which is therefore made in the invention.

The aqueous phase

All types of water are suitable for the production of the O/W-emulsion fluids according to the invention. These can therefore be based on fresh water and in particular also on salt water - particularly sea water here in off-shore wells.

Additives in the emulsion fluid

In principle, all the additives provided for comparable drilling fluid types can be considered, which are usually added in connection with a quite specific desired range of properties for the drilling fluid. The additives can be water-soluble, oil-soluble and/or water- or oil-dispersible.

Classical additives for water-based O/W-emulsion fluids can be: emulsifiers, fluid-loss additives, structure-viscosity-building soluble

and/or insoluble substances, alkali reserves, agents for the inhibition of undesired water-exchange between drilled formations - e.g. water-swellable clays and/or salt strata - and the water-based drilling fluid, wetting agents for better adhesion of the emulsified oil phase to solid surfaces, e.g. for improving the lubricating effect, but also for the improvement of the oleophilic seal of exposed rock formations, or rock surfaces, disinfectants, e.g. for inhibiting bacterial attack on such O/W-emulsions, and the like. For details, reference should be made here to the relevant prior art, as described in detail in the specialist literature cited above, refer here in particular to Gray and Darley, loc. cit., Chapter 11, "Drilling Fluid Components". We will therefore only cite extracts below:

Finely-dispersed additives for increasing the fluid density: Barium sulfate (barite) is widely used, but also calcium carbonate (calcite) or the mixed carbonate of calcium and magnesium (dolomite).

Agents for building up the structure-viscosity, which at the same time also act as fluid-loss additives: Bentonite should primarily be mentioned here which is known to be used in water-based fluids in a non-modified form and is therefore ecologically safe. For salt-water fluids other comparable clays, in particular attapulgite and sepiolite, are of considerable significance in practice.

The additional use of organic polymer compounds of natural and/or synthetic origin can also be of considerable importance in this context. The following are in particular to be mentioned here: starch or chemically modified starches, cellulose derivatives, such as carboxymethylcellulose, guar gum, xanthan gum, or also purely synthetic water-soluble and/or water-dispersible polymer compounds, in particular of the type of the polyacrylamide compounds of high molecular weight with or without anionic or cationic modification.

Thinners for viscosity-regulation: The so-called thinners can be of organic or inorganic nature; examples of organic thinners are tannins and/or quebracho extract. Further examples are lignite and lignite derivatives, particularly lignosulfonates. As indicated above, in a preferred embodiment of the invention the use of toxic components is

particularly to be excluded, and here particularly the corresponding salts with toxic heavy metals, such as chromium and/or copper, are to be mentioned. Examples of inorganic thinners are polyphosphate compounds.

Emulsifiers: For the teaching according to the invention, in particular two features are to be considered here. It has emerged that a stable dispersion of alcohols and in some cases of ester oils is very much more easily possible than the corresponding dispersion of pure mineral oils as used in the state of the art. This already is a first simplification. Furthermore, it should be considered that by the partial saponification of the ester oils under the additional effect of suitable alkali reserves, when longer-chain carboxylic acid esters are used effective O/W-emulsifiers are also formed and contribute to the stabilization of the system.

Additives which inhibit undesired water-exchange with, for example, clays: The additives known from the state of the art for water-based drilling fluids can be considered here. In particular halides and/or carbonates of the alkali and/or alkaline-earth metals, with particular importance given to corresponding potassium salts, optionally in combination with lime. Reference is made for example to the corresponding publications in "Petroleum Engineer International", September 1987, 32 - 40 and "World Oil", November 1983, 93 -97.

Alkali reserves: inorganic and/or organic bases adapted to the total behavior of the fluid can be considered, in particular corresponding basic salts or hydroxides of alkali and/or alkaline-earth metals and organic bases.

In the field of organic bases, a conceptual distinction must be drawn between water-soluble organic bases - for example, compounds of the diethanolamine type - and practically water-insoluble bases of marked oleophilic character as described in the Applicant's co-pending Application 2,009,689 cited above as additives in invert drilling muds based on ester oil. The use of such oil-soluble bases in the framework of the present invention in particular falls within the new teaching. Oleophilic bases of this type, which are distinguished

in particular by at least one longer hydrocarbon radical with, for example, 8 to 36 carbon atoms, are, however, not dissolved in the aqueous phase, but in the dispersed oil phase. Here these basic components are of multiple significance. On the one hand they can act immediately as alkali reserves. On the other, they give the dispersed oil droplets a certain positive state of charge and therefore result in increased interaction with the negative surface charges which can be found in particular in hydrophilic clays which are capable of ion-exchange. According to the invention one can thus influence the hydrolytic cleavage and the oleophilic sealing of water-reactive rock strata.

The amount of auxiliary substances and additives used in each case moves essentially within the usual boundaries and can therefore be found in the cited relevant literature.

Examples

Firstly, a 6% by weight homogenized bentonite suspension is prepared using commercially available bentonite (not hydrophobized) with tap water, and adjusting a pH value of 9.2 to 9.3 by means of sodium hydroxide solution.

Starting with this pre-swollen aqueous bentonite phase, in successive stages of the process - each under intensive intermixing - the individual components of the water-based emulsion according to the following formulation are incorporated:

350 g	6 % by weight bentonite solution
1.5 g	industrial carboxymethylcellulose low-viscosity (Relatin™ U 300 S9)
35 g	sodium chloride
70 g	oleophilic alcohol (according to the definition given below)
1.7 g	emulsifier (sulf. castor oil "Turkey-red oil")
219 g	barite

Viscosity measurements were carried out on the thus prepared O/W-emulsion fluids as follows:

Firstly, the plastic viscosity (PV), the yield point (YP) and the gel strength after 10 sec. and after 10 min. of the emulsion fluid is determined at 50°C on the unaged material.

Following this, the emulsion fluid is aged for 16 hours at 125°C in an autoclave in the so-called "roller-oven", to examine the effect of temperature on the stability of the emulsion. Then, the viscosity values at 50°C were determined once again. In the following examples in each case the nature of the oleophilic alcohol used, the values determined for the unaged and aged material and - if necessary - general comments are given.

Example 1

Oil phase used: isotridecylalcohol

	unaged material	aged material
plastic viscosity [mPa.s]	14	14
yield point [Pa]	20.1	14.4
gel strength [Pa]		
10 sec.	15.8	11.5
10 min.	15.3	18.7

Example 2

The formulation of Example 1 is repeated, but without using the emulsifier (Turkey-red oil).

The viscosity values measured on the unaged and aged material are the following:

	unaged material	aged material
plastic viscosity [mPa.s]	9	10
yield point [Pa]	17.7	18.7
gel strength [Pa]		
10 sec.	16.8	16.8
10 min.	15.8	17.7

Even in the fresh formulation a slight droplet formation can be seen on the surface.

Example 3

Oil phase used: C_{10}-synthetic alcohol (Etoxos™ C10)

The viscosity values measured on the unaged and the aged drilling fluid are as follows:

	unaged material	aged material
plastic viscosity [mPa.s]	16	15
yield point [Pa]	12.9	19.6
gel strength [Pa]		
10 sec.	11.5	13.9
10 min.	18.2	35.4

Example 4

The formulation in Example 3 is repeated using a C_{12-18}-alcohol of natural origin (commercial product Lorol™ techn.). The viscosity values measured on the unaged and aged drilling fluid are as follows:

	unaged material	aged material
plastic viscosity [mPa.s]	9	21
yield point [Pa]	14.4	16.8
gel strength [Pa]		
10 sec.	8.6	14.8
10 min.	8.6	17.7

CLAIMS:

1. A water-based, oil-in-water emulsion drilling fluid suitable for the ecologically-acceptable development of geological formations, comprising:

A) a continuous aqueous phase containing from about 5 to about 50% by weight of an oil phase dispersed in said aqueous phase, based on the weight of said oil phase and said aqueous phase, said oil phase comprising a substantially water-insoluble, oleophilic mono- or polyfunctional alcohol which has a flash point of above about 80°C;

B) an emulsifier;

C) a fluid-loss additive;

D) a weighting agent;

E) a viscosifier; and

F) an alkali reserve component.

2. The water-based, oil-in-water emulsion drilling fluid as in claim 1 wherein said oil phase is present in an amount of from about 8 to about 40% by weight.

3. The water-based, oil-in-water emulsion drilling fluid as in claim 1 or 2 further comprising an ecologically-acceptable, water-insoluble oil comprising an ester oil of a monocarboxylic acid and a mono- or polyfunctional alcohol.

4. The water-based, oil-in-water emulsion drilling fluid as in claim 3 wherein said ecologically acceptable, water-insoluble oil comprises an ester oil of a monocarboxylic acid and a polyfunctional alcohol containing up to 4 hydroxyl groups.

5. The water-based, oil-in-water emulsion drilling fluid as in claim 3 wherein said ester oil is selected from the group consisting of:

(a) an ester of a C_1-C_5 monocarboxylic acid and a mono- or polyfunctional alcohol, wherein said

monofunctional alcohol contains at least 6 carbon atoms and said polyfunctional alcohol contains from 2 to 6 carbon atoms;

(b) an ester of a C_6-C_{16} aliphatically-saturated monocarboxylic acid and a mono- or polyfunctional alcohol, wherein said monofunctional alcohol contains at least 6 carbon atoms and said polyfunctional alcohol contains from 2 to 6 carbon atoms; and

(c) an ester of a C_{16}-C_{24} mono- or polyolefinically unsaturated monocarboxylic acid and a monofunctional alcohol containing at least 6 carbon atoms.

6. The water-based, oil-in-water emulsion drilling fluid as in claim 5 wherein said component (c) is selected from (C1) an ester containing at least about 45% by weight of a di- or polyolefinically unsaturated C_{16}-C_{24} monocarboxylic acid, and (C2) an ester containing less than about 35% by weight of a di- or polyolefinically unsaturated C_{16}-C_{24} monocarboxylic acid and at least about 60% by weight of mono-olefinically unsaturated C_{16}-C_{24} monocarboxylic acid.

7. The water-based, oil-in-water emulsion drilling fluid as in any one of claims 1 to 6 further comprising up to about 10% by weight, based on the weight of said oil phase, of an oleophilic basic amine having limited solubility in water, wherein said amine is free from aromatic constituents, and has at least one long-chain hydrocarbon radical containing 8 to 36 carbon atoms.

8. The water-based, oil-in-water emulsion drilling fluid as in any one of claims 1 to 7 having a pH of from about 7.2 to about 11.

9. The water-based, oil-in-water emulsion drilling fluid as in any one of claims 1 to 8 wherein said water-insoluble, oleophilic mono- or polyfunctional alcohol constitutes at least about 10% by weight of said oil phase.

10. The water-based, oil-in-water emulsion drilling fluid as in any one of claims 1 to 9 further comprising partial ethers of said polyfunctional alcohol.

11. The water-based, oil-in-water emulsion drilling fluid as in any one of claims 1 to 10 wherein said water-insoluble, oleophilic mono- or polyfunctional alcohol is free from aromatic constituents.

12. The water-based, oil-in-water emulsion drilling fluid as in any one of claims 1 to 11 wherein said monofunctional alcohol contains at least 6 carbon atoms and up to about 36 carbon atoms.

13. The water-based, oil-in-water emulsion drilling fluid as in any one of claims 1 to 12 wherein said oil phase further comprises an oleophilic diol having hydroxyl groups in the alpha and omega positions or on adjacent carbon atoms, or partial ethers thereof.

14. The water-based, oil-in-water emulsion drilling fluid as in any one of claims 1 to 13 wherein said oil phase further comprises a substantially water-insoluble polyalkyleneglycol ether.

15. The water-based, oil-in-water emulsion drilling fluid as in claim 14 wherein said ether is selected from the group consisting of a lower alkylene glycol ether, and a mixed ether of ethylene oxide, propylene oxide, or mixtures thereof having at least one free hydroxyl group.

16. The water-based, oil-in-water emulsion drilling fluid as in any one of claims 3 to 6 wherein said ester oil has a Brookfield (RVT) viscosity of up to about 2 million mPas at about 20°C.

17. A process of developing a source of petroleum, natural gas or water by drilling, comprising drilling said source in the presence of a drilling fluid as in any one of claims 1 to 16.